

Organochlorine Pesticides in the Surface Waters from Sharda River Region, Uttar Pradesh-India

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Abstract—This study reports the concentration levels and distribution patterns of the 21 organochlorine pesticide residues in the surface water of Sharda river region in Lakhimpur kheeri, Uttar Pradesh-India. Solid Phase Extraction (SPE) is used for the extraction of organochlorine pesticide residues in water sample. In all samples pesticide residues were analyzed by GC (Shimadzu 2010) with Ni⁶³ ECD detector. The residues were further confirmed on Gas Chromatograph-Mass Spectrometer-Quadrupole on Electron Ionization (EI) mode. The most commonly encountered Organochlorine pesticides in surface water were dieldrin, heptachlor epoxide, isomers of hexachlorocyclohexane and DDT. In some cases the concentrations detected were higher than the quantitative target levels set by the European Union, especially for γ -hexachlorocyclohexane & pp'-DDT. The concentration levels found are lower than the EU maximum acceptable concentration of 0.10 $\mu\text{g l}^{-1}$ for all compounds examined, except for δ -HCH in seven samples (0.2772, 0.1950, 0.2210, 0.2045, 0.1994, 0.1523, 0.1390 $\mu\text{g l}^{-1}$) and four samples (0.1877, 0.2365, 0.1478, 0.1269 $\mu\text{g l}^{-1}$) of pp'-DDT during 2008-2010. The occurrence of these compounds in Sharda river region surface waters can be attributed to intense agricultural activity as well as to transboundary pollution.

Keywords—EEC, EU, GC-ECD, LOD, OCPs, SPE, Surface Water

Abbreviations—Certified Reference Material (CRM), European Union (EU), Limit Of Detection (LOD), Organo-Chlorine Pesticides (OCPs), Solid Phase Extraction (SPE)

I. INTRODUCTION

ORGANOCHLORINE Pesticides (OCPs) are ubiquitous and persistent organic pollutants used widely throughout the world. Due to the extensive use in agriculture, organic environmental contaminants such as HCH, DDT along with other organochlorine pesticides are distributed globally by transport through air and water. Organochlorine pesticides are insecticides composed primarily of carbon, hydrogen and chlorine. They break down slowly and can remain in the environment a long after application and in organisms long after exposure. OCPs, with their high degree of toxicity, constitute a very important group of target compounds in environmental samples. Because of their widespread use, they are detected by determination of their residues in various environmental matrices, such as soil, water, milk and air. Those present in waters may have an agricultural, domestic, or industrial origin, the most harmful effect being their inclusion in the so-called "nutrition chain". Environmental pollution by pesticides is a major environmental concern [López et al.,

2001; Vinas et al., 2002]. Organochlorine pesticides are known to resist biodegradation and therefore they can be concentrated through food chains and original concentration at the end of the chain [Sankaramakrishnan et al., 2005]. Pesticides are one class of compounds that, despite their benefits, may produce a wide range of toxic side effect that pose a potential hazard to the environment [Golfinopoulos et al., 2003]. While pesticides are indispensable in modern agriculture, their use or misuse may lead to serious water quality problems [Wauchope et al., 1994; El-Kabbany et al., 2000]. Pesticide contamination surface and ground waters from agricultural use has been well documented around the world [Wauchope et al., 1994; Hairston et al., 1995]. Many Organochlorine Pesticides (OCPs) were used on a global scale from the 1950s to the mid 1980s, most of which are stable and persistent in the environment. Usage of OCPs has been prohibited in most countries including India [Barra et al., 2001; Turgut 2003]. Although drinking water contamination from pesticides is rare, it is possible under certain conditions. In India, largest pesticide consumption has been in the state of Uttar Pradesh, according to the data of

1995-1996 and 1999-2000, produced by Central Insecticide Board and Registration Committee, India [Srivastava et al., 2008; Besbelli, 1998]. An extremely toxic pesticide can cause the death of fish and other aquatic organisms even at low concentration. They have been reported to alter various reproduction functions in various animals including marine populations. Most surface waters (except deep lakes) have a rapid turn over rate, which means that fresh water dilutes the concentration of the contaminant quickly. In addition, most surface waters contain free oxygen, which enhances the rate at which pesticides are broken down by microorganisms. Pesticides applied immediately before a heavy rain may wash into streams or other surface waters and threaten fish and wildlife. For these reasons, usage of pesticides directly around a drinking water source would be forbidden [Bonner 1993; Pesando et al., 2004]. The success of raw water treatment should be examined by pesticide monitoring of the distributed potable water. Certain kinds of older pesticides, such as γ -HCH which may contain persistent α - and β -isomers are still present in the agricultural and could cause the residue problem. Pesticides sorbed to particulates are transported by streams and surface waters [Aydın & Yurdun, 1999]. Monitoring studies in European and Asian countries have shown widespread detection of pesticides in ground and surface water. The levels of pesticides detected in water depend largely on the intensity of agricultural production in a given region. As the council directive 80/778 of the European Union (EU) limits the concentration of individual pesticide and toxic transformation products in drinking water to $0.10 \mu\text{g l}^{-1}$ and the total concentration to $0.50 \mu\text{g l}^{-1}$, many methods have been developed for both sample preparation and chromatographic separation and detection. The most common methods of preconcentration of various classes of pesticides from water samples are liquid-liquid extraction and solid-phase extraction [Vassilakis et al., 1998]. Solid-phase extraction is a rapidly growing sample preparation method, used most frequently for extracting trace organics in aqueous matrices, prior to injection into a gas chromatography. C-18 SPE has been used in studies of specific materials such as trace metals, individual organic compounds, and pesticides as well as investigations into natural organic matter. Analytical methods for pesticide residues have their main application in the control of food for human consumption, especially in the control of fruit or vegetables and drinking waters since they are generally produced using direct application of pesticides [Nerin et al., 1998; Simjouw et al., 2005]. Rural population may be exposed to pesticides in several ways: by spraying into the air and ingestion of pesticide residues via food and drinking water. Some pesticides are characterized by being very persistent in the environment. They may represent long-term dangers as they biomagnify up the food chain, Humans, and particularly breastfed babies, are at the top of food chain. There is concern about potential endocrine and developmental effects of the pesticides, especially in children. Information OCPs in sources of drinking water from Sharda River Region in Lakhimpur Kheeri (Uttar Pradesh-India) is not available. These studies describe the

organochlorine pesticide result in surface waters from Sharda River Region in Lakhimpur Kheeri which takes place in the Terai-belt of Uttarpradesh-India, Sharda River Region, main sources of drinking water are the surface waters. Palia Kalan, Bhera and Bhanpur Khajuria areas take place in this region. Due to high annual rainfall in the region, floods result in transport of contaminants from agricultural areas to surface waters. The objective of the present study was to carry out the levels of various organochlorine pesticide residues in surface waters.

II. MATERIAL AND METHODS

2.1. Site

Lakhimpur Kheri ($28^{\circ} 27' 0''$ North, $80^{\circ} 35' 0''$ East) is a largest district in terms of area (Total Area = 7680 sq km) in Uttar Pradesh, India, on the border with Nepal. Sugarcane, wheat, pulses, oilseeds, rice, and potatoes are grown and processed in this district, forming the backbone of the local economy. Some of India's largest sugar mills are in the district. Bajaj sugar mill in Gola Gokarnathand, Bajaj sugar mill in Palia Kalan and Kishan Sarkari mill in Sampurnanagar are the three largest sugar mills in Asia.

2.2. Sampling

For this study, random sampling technique was applied, all the samples were collected in high purity glass bottles from three different location of Sharda river region for a period of 3 years and refrigerated at 4°C until analysis. A study was conducted in three areas of Lakhimpur Kheri namely Palia Kalan (B 1, B 2, B 3), Bhera (B 4, B 5, B 6) and Bhanpur Khajuria (B 7, B 8, B 9). A total of 27 surface water samples at the water surface of Sharda River Region were collected from agricultural area. Yearly variations of pesticide detections in surface water according to the timing of pesticide applications related to sampling intervals have been noticed. Winter months were chosen for sampling because pesticide detections tended to be more frequent and more concentrated during winter seasons. At each location, samples were collected by strapping two 1-l glass bottles. The vials were carefully filled just by overflowing, without passing air bubbles through samples or trapping air bubbles in sealed bottles. Preparation of vials included washing with detergent, rinsing with tap water then ultra-pure water, and air-dried. All samples were filtered through $0.45\text{-}\mu\text{m}$ nylon filter to remove sand and debris, acidified with hydrochloric acid (6N) to pH 2.5 after returning to the laboratory and extracted immediately.

Table 1 – Concentrations of Organochlorine Pesticides Detected in the Surface Water Samples from the Sharda River Region in 2008

Organochlorine Pesticide	Concentration ($\mu\text{g l}^{-1}$)								
	Palia Kalan			Bhera			Bhanpur Khajuria		
	B-1	B-2	B-3	B-4	B-5	B-6	B-7	B-8	B-9
α -HCH	ND	0.0052	ND	ND	ND	ND	0.0041	ND	0.0039
β -HCH	ND	ND	ND	0.0062	ND	ND	ND	0.0095	ND
γ -HCH	0.2772	ND	ND	0.1950	ND	ND	ND	0.2210	ND
δ -HCH	ND	ND	ND	ND	ND	ND	ND	ND	ND
Heptachlor	ND	ND	ND	ND	ND	ND	ND	ND	ND
Aldrin	ND	ND	ND	ND	ND	ND	ND	ND	ND
Heptachloreoxide	ND	ND	ND	ND	ND	ND	ND	ND	ND
α -Chlordane	ND	ND	ND	ND	ND	ND	ND	ND	ND
Trans-chlordane	ND	ND	ND	ND	ND	ND	ND	ND	ND
α -Endosulfane	ND	ND	ND	ND	ND	ND	ND	ND	ND
β -Endosulfan II	ND	ND	ND	ND	ND	ND	ND	ND	ND
p,p-DDE	ND	ND	ND	ND	ND	ND	ND	ND	0.0047
p,p-DDD	ND	ND	ND	ND	ND	ND	ND	ND	ND
p,p-DDT	0.1877	ND	ND	0.2365	ND	ND	ND	ND	ND
Endrin	ND	ND	ND	ND	ND	ND	ND	ND	ND
Diendrin	ND	ND	ND	ND	ND	ND	ND	ND	ND
Endrin aldehyde	ND	ND	ND	ND	ND	ND	ND	ND	ND
Endosulfan sulfate	ND	ND	ND	ND	ND	ND	ND	ND	ND
Methoxychlor	ND	ND	ND	ND	ND	ND	ND	ND	ND
Endrin Ketone	ND	ND	ND	ND	ND	ND	ND	ND	ND
Hexachlorobenzene	ND	ND	ND	ND	ND	ND	ND	ND	ND

European Economic Commission Standards (EEC Council Directive 1980/778/EEC) for drinking water: the total pesticide level should not exceed $0.50 \mu\text{g l}^{-1}$ and individual pesticide should not be greater than $0.10 \mu\text{g l}^{-1}$.

ND not detected

2.3. Analyte Recovery and Quality Control

Water samples were spiked 0.002 , 0.003 and $0.005 \mu\text{g l}^{-1}$, 5 mL of methanol added and passed through a 6 mL capacity C18 cartridge. The cartridge was optimized with 5 mL of ethylacetate, 5 mL of dichloromethane, 10 mL of methanol and 10 mL of organic free water before use. Then it was eluted with extraction solvent (Dichloromethane: hexane; 3:1). The recovery experiment was performed at the three concentrations and each concentration was analyzed in triplicate. Recoveries were obtained from 80 ± 2.43 to 110 ± 4.65 % across the three concentrations. The Limit Of Detection (LOD) and Limit Of Quantification (LOQ) for OCPs was $0.001 \mu\text{g l}^{-1}$ and $0.002 \mu\text{g l}^{-1}$, respectively.

2.4. Extraction of the Sample

Solid Phase Extraction (SPE) is used for the extraction of organochlorine pesticide residues in water sample. The collected water samples were pre-filtered through a $0.45 \mu\text{m}$ nylon filter (Wattman) to remove particulate matter and were acidified with hydrochloric acid (6N) to pH 2.5. Methanol modifier (BDH, for pesticide residue analysis, 10 mL) was added to water sample for better extraction. SPE using pre-packed reversed phase octadecyl (C-18 bonded silica) contained in cartridges was used for sample preparation. Prior to the extraction, the C-18 bonded phase, which contains 500 mg of bonded phase, was optimized with 5 mL of ethylacetate, 5 mL of dichloromethane, 10 mL of methanol and 10 mL of organic free water before use. The sample was mixed well and allowed to percolate through the cartridges

with flow rate of 10–15 mL/min under vacuum. After sample extraction, suction continued for 15 min to dry the packing material and pesticides trapped in the C-18 bonded phases were eluted by passing 10 mL extraction solvent (Dichloromethane : hexane; 3:1) and fraction was evaporated in a gentle steam of Nitrogen. Final volume was made up into 1 ml by n-hexane and injected $1 \mu\text{l}$ in gas liquid chromatograph equipped with an electron capture detector (Ni^{63}). The residues were further confirmed on Gas Chromatograph-Mass Spectrometer-Quadrupole on Electron Ionization (EI) mode.

III. EXPERIMENTAL

3.1. GC Instrument

The residues were quantitatively analyzed on Gas Chromatograph-Shimadzu 2010 (Shimadzu, Kyoto, Japan) equipped with split/splitless auto-injector model AOC-20i. The non-polar stationary phase used was a fused silica capillary column DB-5 (5 % phenyl polysiloxane) of 30 m, 0.25 mm i.d. , and $0.25 \mu\text{m}$ film thickness (J&W Agilent Palo Alto, CA, USA). GC Solution software was used for instrument control and data analysis.

3.2. GC/MS Instrument

The residues were further confirmed on Gas Chromatograph-Mass Spectrometer-Quadrupole on Electron Ionization (EI) mode (Shimadzu 2010, Kyoto, Japan) equipped with split/splitless auto-injector model AOC-20i. The non-polar stationary phase used was a fused silica capillary column DB-

1 (1 % phenyl polysiloxane) of 30 m, 0.25 mm i.d., and 0.25 μm film thickness purchased from J&W Agilent Palo Alto, CA, USA. GCMS Solution software was used for instrument control and data analysis.

3.3. Turbo-Vap

Zymark Turbo Vap^(R), LV evaporator (Caliper Life Sciences, USA) was used to concentrate the sample.

3.4. Liquid Dispensers

Liquid dispensers (Labmax, Witeg Germany, 100 mL) to dispense solvent from the bottle to the samples was used. An adjustable pipette (1mL to 5mL, Finnpiquette, Thermo Scientific) was used to transfer the solvent and sample extract to autosampler vials for residues analysis.

Table 2 – Concentrations of Organochlorine Pesticides Detected in the Surface Water Samples from the Sharda River Region in 2009

Organochlorine Pesticide	Concentration ($\mu\text{g l}^{-1}$)								
	Palia Kalan			Bhera			Bhanpur Khajuria		
	B-1	B-2	B-3	B-4	B-5	B-6	B-7	B-8	B-9
α -HCH	0.0086	ND	ND	ND	ND	0.0056	ND	ND	ND
β -HCH	ND	0.0038	ND	ND	ND	ND	ND	ND	ND
γ -HCH	ND	ND	ND	0.2045	ND	ND	ND	0.1994	ND
δ -HCH	ND	ND	ND	ND	ND	ND	ND	ND	ND
Heptachlor	ND	ND	ND	ND	ND	ND	ND	ND	ND
Aldrin	ND	ND	ND	ND	ND	ND	ND	ND	ND
Heptachloreoxide	0.0035	ND	ND	ND	ND	ND	ND	ND	ND
α -Chlordane	ND	ND	ND	ND	ND	ND	ND	ND	ND
Trans-chlordane	ND	ND	ND	ND	ND	ND	ND	ND	ND
α -Endosulfane	ND	ND	ND	ND	ND	ND	ND	ND	ND
β -Endosulfan II	ND	ND	ND	ND	ND	ND	ND	ND	ND
p,p-DDE	0.0068	ND	ND	ND	ND	ND	ND	ND	ND
p,p-DDD	ND	ND	ND	ND	ND	0.0045	ND	ND	ND
p,p-DDT	ND	ND	ND	0.1578	ND	ND	ND	ND	ND
Endrin	ND	ND	ND	ND	ND	ND	ND	ND	ND
Diendrin	ND	ND	ND	ND	ND	ND	ND	ND	0.0029
Endrin aldehyde	ND	ND	ND	ND	ND	ND	ND	ND	ND
Endosulfan sulfate	ND	ND	ND	ND	ND	ND	ND	ND	ND
Methoxychlor	ND	ND	ND	ND	ND	ND	ND	ND	ND
Endrin Ketone	ND	ND	ND	ND	ND	ND	ND	ND	ND
Hexachlorobenzene	ND	ND	ND	ND	ND	ND	ND	ND	ND

European Economic Commission Standards (EEC Council Directive 1980/778/EEC) for drinking water: the total pesticide level should not exceed $0.50 \mu\text{g l}^{-1}$ and individual pesticide should not be greater than $0.10 \mu\text{g l}^{-1}$.

ND not detected.

3.5. Analytical Balance

An electronic weighing balance (Globuz) with digital display was used to weigh the reagents.

3.6. Vials and Vessel

GC autosampler (1.5 mL) vials with septa were used for the final extracts.

IV. REAGENTS

4.1. Dichloromethane, Ethylacetate, Methanol & n-Hexane

Organic solvents were of good quality for pesticide residue analysis and were obtained from Merck (Darmstadt, Germany).

4.2. Pesticide Standards

The Certified Reference Material (CRM) for the residue analysis was obtained from Sigma-Aldrich/ Riedel-de-Haen (Zwijndrecht, The Netherlands).

4.3. Preparation of Standard Solutions

Individual stock solutions ($1000 \mu\text{g mL}^{-1}$) of pesticide standards were prepared by dissolving 25 mg in 25 mL toluene and n-hexane in the ratio (1:1) in volumetric flask. Each pesticide was successively diluted up to 200, 20, 2 and $1 \mu\text{g mL}^{-1}$. Standard solution of pesticide mixture of $5 \mu\text{g mL}^{-1}$ was prepared in n-hexane by mixing each of pesticide in appropriate proportion and the solution (pesticide mixture) was serially diluted to 1, 0.5, 0.1, 0.05, 0.01 and $0.005 \mu\text{g mL}^{-1}$ n-hexane for the calibration, USA. GC-MS Solution software was used for instrument control and data analysis.

Table 3 – Concentrations of Organochlorine Pesticides Detected in the Surface Water Samples from the Sharda River Region in 2010

Organochlorine Pesticide	Concentration ($\mu\text{g l}^{-1}$)								
	Palia Kalan			Bhera			Bhanpur Khajuria		
	B-1	B-2	B-3	B-4	B-5	B-6	B-7	B-8	B-9
α -HCH	ND	0.0023	ND	ND	ND	ND	ND	ND	ND
β -HCH	ND	ND	ND	ND	ND	ND	ND	ND	ND
γ -HCH	ND	0.1523	ND	ND	ND	0.1390	ND	ND	ND
δ -HCH	ND	ND	ND	ND	ND	ND	ND	ND	ND
Heptachlor	ND	ND	ND	ND	ND	ND	ND	ND	ND
Aldrin	ND	ND	ND	ND	ND	ND	ND	ND	ND
Heptachlorepoixide	ND	ND	ND	ND	ND	ND	ND	ND	ND
α -Chlordane	ND	ND	ND	ND	ND	ND	ND	ND	ND
Trans-chlordane	ND	ND	ND	ND	ND	ND	ND	ND	ND
α -Endosulfane	ND	ND	ND	ND	ND	ND	ND	ND	ND
β -Endosulfan II	ND	ND	ND	ND	ND	ND	ND	ND	ND
p,p'-DDE	ND	0.0034	ND	ND	ND	ND	ND	ND	0.0047
p,p'-DDD	ND	ND	ND	ND	ND	ND	ND	ND	ND
p,p'-DDT	ND	ND	ND	ND	ND	0.1269	ND	ND	ND
Endrin	ND	ND	ND	ND	ND	ND	ND	ND	ND
Diendrin	ND	ND	ND	ND	ND	ND	ND	ND	ND
Endrin aldehyde	ND	ND	ND	ND	ND	ND	ND	ND	ND
Endosulfan sulfate	ND	ND	ND	ND	ND	ND	ND	ND	ND
Methoxychlor	ND	ND	ND	ND	ND	ND	ND	ND	ND
Endrin Ketone	ND	ND	ND	ND	ND	ND	ND	ND	ND
Hexachlorobenzene	ND	ND	ND	ND	ND	ND	ND	ND	ND

European Economic Commission Standards (EEC Council Directive 1980/778/EEC) for drinking water: the total pesticide level should not exceed $0.50 \mu\text{g l}^{-1}$ and individual pesticide should not be greater than $0.10 \mu\text{g l}^{-1}$.

ND not detected.

V. RESULTS AND DISCUSSION

The concentrations of organochlorine pesticides (OCPs), including α -, β -, γ -, and δ -hexachlorocyclohexane (HCH), heptachlor, heptachlor epoxide, dieldrin, aldrin, endrin, endrin aldehyde, endosulfan I, endosulfan II, endosulfan sulfate, p,p'-DDE, p,p'-DDD, p,p'-DDT, methoxychlor, Heptachlordane, Transchlordane & Endrin ketone determined to evaluate the level of contamination during 2008-2010. Out of 27 samples, 15 were found to be contaminated with DDT and HCH residues *viz.* o,p'-DDT, p,p'-DDT, p,p'-DDE, α -HCH, β -HCH and γ -HCH. In 2009, only two samples were contaminated with heptachlorepoixide & Dieldrin. The highest DDT & HCH residues were recorded in 2008 followed with 2009 & 2010. Among all the components of DDT and HCH, p,p'-DDT & γ -HCH were present in major amount in the contaminated samples. The contribution of o,p'-DDT, p,p'-DDT, p,p'-DDE, α -HCH, β -HCH, γ -HCH, heptachlorepoixide & Dieldrin were 66.67 % (2008), 66.67 % (2009) and 33.33 % (2010) to the total samples. Results of sample analyses are summarized in Tables 1, 2 and 3. These analyses were carried out on samples from different localities and various surface waters in Sharda River Region. It is well known that most of the applied pesticides are subject to many transport and conversion product. air drift, or surface runoff affecting abundance and diversity of non-target species producing complex effects on the ecosystems and altering tropic interactions [Sankaramakrishnan et al., 2005]. Throughout the studied period, the γ -HCH was present in three samples of 2008 (B-1; 0.2772, B-4; 0.1950, B-8; 0.2210

$\mu\text{g l}^{-1}$) followed by two samples of 2009 (B-4; 0.2045, B-8; 0.1994 $\mu\text{g l}^{-1}$) and two samples of 2010 (B-2; 0.1523, B-4; 0.1390 $\mu\text{g l}^{-1}$). The pp'-DDT was present two samples of 2008 (B-1; 0.1877, B-4; 0.2365 $\mu\text{g l}^{-1}$), one sample of 2009 (B-4; 0.1478 $\mu\text{g l}^{-1}$) and one sample of 2010 (B-6; 0.1269 $\mu\text{g l}^{-1}$). In the residue, levels of γ -HCH and pp'-DDT were found to be high as per WHO Guidline, European Economic Commission Standards [EEC Council Directive 1980/778/EEC] and Indian Standard Values for drinking water quality [World Health Organization, 1993]. The highest concentration of $0.2772 \mu\text{g l}^{-1}$ was observed for γ -HCH. α -HCH, β -HCH, o,p'-DDT p,p'-DDE and heptachlor epoxide were present in the lower concentration. Concentration of dieldrin in this study was remarkably lower in comparison to other surface waters [Ayas et al., 1997; Turgut 2003; Golfinoopoulos et al., 2003]. Aldrin and dieldrin are closely related organochlorines. They were involved in numerous incidents of wildlife mortality. When aldrin is applied in the field, it is rapidly broken down to dieldrin [Turgut, 2003]. These results demonstrate that there existed certain potential health risks to drinking water consumer in Sharda River Region. The sources of OCP residues in the surface waters studied are agricultural practices within the region, in combination with rainfall. HCH isomers are the pesticides most frequently reported in previous studies of surface waters. The water level and the time of season's transformation also alter in each year due to the difference in the amount of rainfall and the climate around the surface waters [Geyikçi & Büyüküngör, 2002]. The high concentration of OCPs in the surface water could be attributed to the agricultural runoff resulting from the

extensive agricultural activity in the banks of these locations. OCPs as a certain class of persistent organic pollutants have long biochemical half-lives in the environment. For instance, the biochemical half-life of DDT in the environment is at least 15 years. The persistent nature of OCPs and their translocation from agricultural land as runoff or as irrigation return flow can cause residues in water sources [Matin et al., 1998]. In India, groundwater levels are high and soils are usually coarse, which probably contribute to pesticide pollution of groundwater. It will take time for residues to decline in groundwater or to stop being leached into surface water [Geyikçi & Büyükgüngör, 2002]. A monitoring in Sharda River Region showed that significant amounts of OCPs are detected in surface waters. DDT compounds had been banned in many countries including India [Turgut, 2003]. Irani et al., (2002) investigated 15 OCP residues in drinking waters around Delhi. They found that organochlorine pesticides in the ground water and irrigation water samples were below the Maximum Contaminant Level as prescribed by WHO, and no organochlorine insecticides were detected in any of the drinking water samples. Turgut (2003) investigated the organochlorine pesticide and heavy metal contaminations in The Kucuk Menderes River of Turkey. He reported that the contamination have remained although these pesticides were banned. He also reported DDT derivatives such as 4, 4' -DDD in high concentration. The highest concentration belonged to heptachlor epoxide (281 ng/L). Shukla et al., (2006) reported that all analyzed drinking water samples of Hyderabad city were found to be contaminated with four pesticides i.e. DDT, beta-Endosulfan, alpha-Endosulfan and Lindane. DDT was found to range between 0.15 and 0.19 $\mu\text{g l}^{-1}$ beta-Endosulfan ranges between 0.21 and 0.87 $\mu\text{g l}^{-1}$ alpha-Endosulfan ranges between 1.34 and 2.14 $\mu\text{g l}^{-1}$ and Lindane ranges between 0.68 and 1.38 $\mu\text{g l}^{-1}$ respectively. These concentrations of pesticides in the water samples were found to be above their respective Acceptable Daily Intake (ADI) values for Humans in Hyderabad city during 2006.

Table 4 – Concentration of DDT and HCH ($\mu\text{g l}^{-1}$) in Water from Various Location in India

Location	DDT	HCH	Reference
Drinking water, Haryana	< 0.150-2.70	2.20-4.00	Kumari et al., (1996)
Rural ponds, Uttar Pradesh	0.620-4.48	0.810-2.94	Dua et al., (1996)
Lakes Jaipur	0.04-47.00	0.01-9.30	Kumar et al., (1988)
Mahala water reservoir, Jaipur	0.220-33.00	0.3-46.00	Bakre et al., 1990

In this study, DDT and HCH were present in major amount for maximum contaminated samples. But results found in this study were remarkably lower to those in other surface/drinking water in India (Table 4). The results of this survey show that the surface waters in the Sharda River Region have particular problems with respect to Organochlorine pesticide residues.

VI. CONCLUSION

The important harmful effect of these pesticides occurs in aquatic systems. They can accumulate in water and then show their toxic effects. This effect causes the decrease of usable waters and has a bad effect on aquatic organisms directly. Because of these effects, water source should be monitored continuously [Sait Bulut et al., 2010]. A number of surface water samples obtained from Sharda River Region were analyzed for presence of organochlorine pesticide residues (Table 1, Table 2, Table 3). The compounds detected were HCH (the isomers α -, β -, and γ -HCH), dieldrin, p,p'-DDD, p,p'-DDE, p,p'-DDT and heptachlor epoxide. Adopting pesticide use procedures that minimize or avoid the possibility of water contamination may mean a change in the usual practices of many pesticide users, but changes, when required, are essential. Levels of pesticides in water resources can be reduced by a regular process which would result with maximum protection of humans and the environment and minimum disruption of food production. Monitoring of the environment (including food, water, biota, soil, and air) for pesticide residues must continue. This work provided the first systemic data on the contamination status of OCPs in surface water of Sharda River Region, Utter Pradesh-India. Due to previous excessive agriculture application, atmosphere transport, and difficulty of degradation, there still existed a variety of OCP residues in the surface waters in Terai-belt. The levels of pesticide residues found ranged widely, from 0.0023 $\mu\text{g l}^{-1}$ to 0.2772 $\mu\text{g l}^{-1}$ for OCPs. The OCPs which have been detected are hexachlorocyclohexane (the isomers α -, β -, and γ -hexachlorocyclohexane), dieldrin, endrin, p, p'-DDD, p, p'-DDE, p, p'-DDT and heptachlor epoxide. The presence of OCPs in water is also attributed to intense agricultural activity in the area of Sharda River Region. Result confirms the presence of OCPs in the surface waters with low concentration. In view of our observations suggest that further investigation on surface water for persistent organochlorine pesticides are needed to elucidate future pollution trends and to assess especially human and children health risk.

REFERENCES

- [1] EEC Council Directive 80/778/EEC (1980), *Official Journal of European Communities*, Vol. 229, Pp.11.
- [2] S. Kumar, R. Lal & P. Bhatnagar (1988), "Residues of Organochlorine Insecticides in Two Lakes of Jaipur, India", *Water Air Soil Pollution*, Vol. 42, Pp. 57–65.
- [3] P.P. Bakre, V. Misra & P. Bhatnagar (1990), "Organochlorine Residues in Water from the Mahala Water Reservoir, Jaipur", *India Environment Pollution*, Vol. 63, Pp. 275–281.
- [4] World Health Organization (1993), *Guidelines for Drinking Water Quality* (2nd ed., Vol. 1.). Recommendations, Geneva, Switzerland.
- [5] D.R. Wauchope, D.B. Baker, K. Balu & H. Nelson, (1994), "Pesticides in Surface and Ground Water", *Agricultural Science and Technology*, Vol. 2, Pp. 159–168.
- [6] J.E. Hairston, T. Balch & J.C. Laprade (1995), "Pesticide Management to Protect Water Quality Understanding

- Pesticides and How they Affect Water Quality”, *Alabama Cooperative Extension Service. Auburn University Alabama wq*, Pp. 4–5.
- [7] B. Kumari, R. Singh, V.K. Madan, R. Kumar, T.S. Kathpal (1996), “DDT and HCH Compounds in Soils, Ponds and Drinking Water of Haryana, India”, *Bull Environ Contam. Toxicol*, Vol. 57, Pp. 787–793.
- [8] V.K. Dua, R. Kumari & V.P. Sharma (1996), “DDT and HCH contamination of rural ponds of India”, *Bull Environ Contam. Toxicol*, Vol. 57: Pp. 568–574
- [9] N. Besbelli (1998), “POPs Related Problems in Turkey”, Proceedings of the Subregional Meeting on National Strategy and Action Plan for Reducing/Eliminating POPs Releases, United Nations Environment Programme (UNEP). Moscow, Russian Federation 3–5.
- [10] J. Bonner (1993), “An Environmental Self-Assessment Handling and Storing Pesticides”, Mississippi State University. Project Number, 1910, Pp. 1–13.
- [11] Z. Ayas, N. Barlas & D. Kolankaya (1997), “Determination of Organochlorine Pesticide Residues in Various Environments and Organisms in Gökusu Delta Turkey”, *Aquatic Toxicology*, Vol. 39, Pp. 171–181.
- [12] Vassilakis, I. Ankara, D. Tsipi & M. Scoullas (1998), “Determination of a Variety of Chemical Classes of Pesticides in Surface and Ground Waters by Off-Line Solid-Phase Extraction, Gas Chromatography with Electron-Capture and Nitrogen-Phosphorus Detection, and High-Performance Liquid Chromatography with Post-Column Derivatization and Fluorescence Detection”, *Journal of Chromatography A*, Vol. 823, Pp. 49–58.
- [13] M.A. Matin, M.R. Malek, S. Amin & J.M. Rahman Khatoon (1998), “Organochlorine Insecticide Residues in Surface and Underground Water from Different Regions of Bangladesh”, *Agriculture, Ecosystems and Environment*, Vol. 69, Pp.11–15.
- [14] C. Nerin, R. Battle & J. Cacho (1998), “Determination of Pesticides in High-Water-Content Samples by Off-Line Supercritical Fluid Extraction–Gas Chromatography–Electron-Capture Detection”, *Journal of Chromatography A*, Vol. 795, Pp.117–124.
- [15] A. Aydın & T. Yurdun (1999), “Residues of Organochlorine Pesticides in Water Sources of Istanbul”, *Water, Air and Soil Pollution*, Vol. 111, Pp. 385–398.
- [16] S. El-Kabbany, M.M. Rashed & M.A. Zayed (2000), “Monitoring of the Pesticide Levels in Some Water Supplies and Agricultural Land, in El-Haram, Giza”, *Journal of Hazardous Materials*, Vol. 72, Pp. 11–21.
- [17] R. Barra, M. Cisternas, R. Urrutia, K. Pozo, P. Pacheco & O. Parra (2001), “First Report on Chlorinated Pesticide Deposition in a Sediment Core from a Small Lake in Central Chile”, *Chemosphere*, Vol. 45, Pp. 749–757.
- [18] F.J. López, E. Pitarch, S. Egea, J. Beltran & F. Hernández (2001), “Gas chromatographic Determination of Organochlorine and Organophosphorus Pesticides in Human Fluids using Solid Phase Microextraction”, *Analytica Chimica Acta*, Vol. 433, Pp. 217–226.
- [19] F. Geyikçi & H. Büyükgüngör (2002), “Organik Klorlu Pestisitlerden Benzen Hegza Klorür Veizomerlerin in yeraltive yüzey sularında olu şturdu ğu kirlili ğin ara ştirılması”, *Çevre Bilimleri*, Vol. 5, Pp.39–46.
- [20] M Irani & G Madhuban (2002), “Organochlorine Insecticide Residues in Drinking Water in and around Delhi”, *Environment Monitoring and Assessment*, Vol. 76, Pp. 93–185.
- [21] P. Vinas, N. Campillo, I. López-García, N. Aguinaga & M. Hernández-Córdoba (2002), “Determination of Pesticides in Waters by Capillary Gas Chromatography with Atomic Emission Detection”, *Journal of Chromatography A*, Vol. 978, Pp. 249–256.
- [22] K.S. Golfinopoulos, D.A. Nikolaou, M.N. Kostopoulou, N.K. Xilourgidis, M.C. Vagi & D.T. Lekkas (2003), “Organochlorine Pesticides in the Surface Waters of Northern Greece”, *Chemosphere*, Vol. 50, Pp. 507–516.
- [23] C. Turgut (2003), “The Contamination with Organochlorine Pesticides and Heavy Metals in Surface Water in Küçük Menderes River in Turkey, 2002–2003”, *Environment International*, Vol. 29, Pp. 29–32.
- [24] D. Pesando, S. Robert, P. Huitorel, E. Gutknecht, L. Pereira & J.P. Girard (2004), “Effects of Metoxychlor, Dieldrin and Lindane on Sea Urchin Fertilization and Early Development”, *Aquatic Toxicology*, Vol. 66, Pp. 225–239.
- [25] N. Sankaramakrishnan, A.K. Sharma & R. Sanghi (2005), “Organochlorine and Organophosphorous Pesticide Residues in Ground Water and Surface Waters of Kanpur, Uttar Pradesh, India”, *Environment International*, Vol. 31, Pp.113–120.
- [26] J. Simjouw, E. Minor & K. Mopper (2005), “Isolation and Characterization of Estuarine Dissolved Organic Matter: Comparison of Ultrafiltration and C-18 Solid Phase Extraction Techniques”, *Marine Chemistry*, Vol. 96, Pp. 219–235.
- [27] G. Shukla, A. Kumar, M. Bhanti, P.E. Joseph & A. Taneja (2006), “Organochlorine Pesticide Contamination of Ground Water in the City of Hyderabad”, *Environment International*, Vol. 32, Pp. 244–247.
- [28] S. Srivastava, S.S. Narvi & S.C. Prasad (2008), “Organochlorines and Organophosphates in Bovine Milk Samples in Allahabad Region”, *International Journal of Environmental Research*, Vol. 2, No. 2, Pp.165–168.
- [29] Sait Bulut, Sevim Feyza Erdogmus, Muhsin Konuk & Mustafa Cemek (2010), “The Organochlorine Pesticide Residues in the Drinking Waters of Afyonkarahisar, Turkey”, *Ekoloji*, Vol. 19, No. 74, Pp. 24–31.



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